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BLEACHING OF CELLULOSE PULP

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This invention relates generally to the bleaching of chemically prepared cellulose pulps and particularly seeks to provide a novel method of obtaining a substantial reduction in viscosity of such pulps at a low cost and without having to vary any of the normal bleaching or purifying sequences or conditions.

Since in the production of bleached chemical pulps for paper it is generally desirable to minimize the viscosity drop in order to retain the necessary strength characteristics in the finished paper, it is unlikely that this invention would be frequently used in connection with paper pulps.

However, in connection with bleached pulps manufactured for other end uses, and particularly those which enter into the production of cellulose derivatives such as viscose rayon or other forms of regenerated cellulose, the degree of polymerization of such pulps must be reduced to a low level before the pulps are converted, and this invention is especially applicable.

The desired viscosity drop (or reduction of the degree of polymerization) has been effected in the past either in the pulp mill during bleaching operations or subsequently in a conversion process through aging of alkali cellulose.

A number of metals, notably manganese and cobalt, have been proposed as catalysts to accelerate the alkaline oxidation of alkali cellulose during aging, and they are usually added to the bleached pulp during the final drying stage. However, it has been found that such aging catalysts build up and recirculate in the caustic system of the manufacturer of viscose rayon or other cellulose derivatives during the initial formation of alkali cellulose giving rise to difficulties in process control. The pulp manufacturer must also take precautions to prevent the build-up of catalysts in the white waters of a pulp drying machine.

Accordingly, there are definite advantages to obtaining a lowering of the pulp viscosity during bleaching rather than subsequently during the conversion process. In the past, however, such bleaching has always involved the expense of extra bleaching agents; production has been lowered by the requirement for longer bleaching times; and equipment troubles frequently have been encountered as the result of the enforced use of higher bleaching temperatures. Therefore, a method of viscosity reduction during pulp bleaching which does not involve these disadvantages is desirable.

Unexpectedly we have discovered that the addition of a small amount of a vanadium compound to the initial chlorination stage of bleaching is very effective in lowering pulp viscosity without involving extra usage of bleaching chemicals or requiring any change in normal processing conditions. Since it is normal pulp mill practice to sewer the spent chlorination liquors the problem of build up of vanadium in the white water system either does not exist or is of such small consequence that it can be readily controlled.

Accordingly, an object of this invention is to provide

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a novel method for reducing the viscosity of cellulose pulp during the chlorination stage of a multi-stage bleaching process without requiring the use of extra bleaching chemicals or any change in normal processing conditions.

A further object of this invention is to provide a process of the character stated in which a small amount of a vanadium compound is added to the initial chlorination stage in order to effect the desired lowering of pulp viscosity.

A further object of this invention is to provide a method of the character stated in which no trace of the vanadium compound remains following the chlorination and alkaline extraction stages in a multi-stage pulp bleaching system.

Chlorination is a necessary step in most pulp bleaching sequences, and its purpose is to render the lignin soluble in a subsequent alkaline stage. The hydrolysis of chlorine in water results in the formation of hypochlorous acid. Elemental chlorine is presumed to react with the lignin in a substitution reaction while the hypochlorous acid acts as an oxidizing agent on both the lignin and the cellulose. It is this latter reaction which results in a lowering of the viscosity, and we have discovered that the lowering of viscosity during a chlorination stage can be catalyzed through the use of a vanadium compound such as sodium vanadate, vanadium pentoxide and ammonium vanadate. The catalytic action of the vanadium compounds is indicated by the fact that solutions of such compounds at suitably low pH's do not in the absence of chlorine cause any drop in pulp viscosity.

The viscosity lowering that accompanies the use of vanadium is greater in the case of hardwoods than softwoods. This is not surprising in view of the greater sensitivity of hardwood pulps to chlorination variables shown for example by the more severe breakdown caused by overchlorination.

The nature of the viscosity-lowering effect can be seen from the table below illustrating the use of various amounts of vanadium. The pulp used was a hardwood-softwood mixture cooked by the sulphite process and having a chlorine demand of 75.5 lbs. chlorine per air dry ton of pulp. Viscosity in this table is expressed according to TAPPI Method T230Sm-50, alpha was determined according to T203m-55, and resin or pitch according to T204m-54. The hot alkali solubility is the percentage of material dissolved when pulp in a slurry of 2% consistency is heated under reflux in 7.14% (77 g.p.l.) NaOH solution for 3 hours at 100±.2° C. Varying amounts of vanadium in the form of the pentoxides were used in a chlorination stage of 25° C. and 3% consistency for one hour. At the end of this time the pulps were washed and then treated with 4.5% NaOH based on pulp at 95° C. and 15% consistency for three hours. Analyses on the pulp after this stage were:

Chlorine, lbs. per air dry ton of pulp	V, p.p.m. on pulp	Residual Chlorine (lbs./air dry ton)	Visc. (cps.)	Alpha Cellulose, Percent	Hot Alkali Solubles, Percent	Resin, Percent
75.5	0	3.1	25.0	92.7	16.3	0.78
75.5	10	3.1	17.3	92.5	18.0	-----
75.5	20	2.7	15.8	92.5	17.9	-----
75.5	30	2.6	15.6	92.3	18.4	-----
75.5	40	2.3	15.3	92.3	18.5	-----
75.5	50	1.8	14.4	91.9	19.0	0.70
75.5	100	1.5	12.7	91.3	20.0	0.76
75.5	200	1.3	11.3	90.7	21.7	0.82
75.5	300	1.2	11.5	90.1	22.5	0.73
75.5	400	1.1	11.7	90.5	21.7	0.67
75.5	500	1.1	11.8	90.8	21.0	0.70

While it might be expected that pulps will vary in their response to the action of vanadium the table

above indicates that vanadium increases in effectiveness up to about 200 p.p.m. It will be noticed that as the amount of vanadium is increased residual chlorine drops. Alternatively when vanadium is present the amount of chlorine consumed by the pulp can be substantially increased while the residual chlorine remains constant. This can be illustrated with the chlorination conditions shown above as follows:

Chlorine, lbs.	V, p.p.m.	Residual Chlorine	Viscosity
75.5	0	3.1	25.0
75.5	100	1.5	12.7
82.0	100	1.5	10.8

With use of vanadium in quantities of the order of 0-50 p.p.m. V, a viscosity drop is obtained with a decrease in alpha and a rise in hot alkali solubility neither of which is excessive compared with levels to be expected from any normal method of viscosity reduction.

The overall rate of reaction during chlorination, as measured by the amount of chlorine consumed in a given time, appears to be increased by the use of vanadium. The substitution portion of the reaction is thought to be quite rapid and unaffected by temperature to a measurable extent while the oxidizing effect of the chlorine requires time and is suppressed to a certain extent at lower temperatures. Both substitution and oxidation are necessary for full and effective chlorination and for this reason chlorinations carried out at low temperatures are not as effective as those at 20-25° C. The use of vanadium should help overcome the deficiency and should also allow chlorination times at normal temperature to be reduced. Both of these possibilities are indicated in the following table which shows chlorine residuals after a chlorination stage at 3% consistency on a sulphite cooked blend of hardwoods and softwoods:

Chlorine, lbs. per air dry ton of pulp	V, p.p.m. on pulp	Temp., ° C.	Time, mins.	Residual Chlorine (lbs./air dry ton)
56	0	25	60	2.5
56	0	10	60	6.3
56	50	10	60	4.9
56	50	25	60	2.3
56	50	25	50	2.3
56	50	25	40	3.1
56	50	25	30	3.3

The following examples also illustrate the practice of the invention:

Example I

A sulphite pulp from a blend of hardwoods and softwoods was chlorinated with 57.5 lbs. chlorine per air dry ton of pulp at 25° C. and 3% consistency for one hour. The chlorine residual was 2.5 lbs./ton. The pulp then received an alkali extraction with 5% NaOH/pulp at 95° C. and 15% consistency for three hours. The viscosity of the pulp after this stage was 22.5 cps. A second sample of the same pulp was treated in an exactly similar fashion excepting that 25 p.p.m. vanadium (added in the form of an aqueous solution of the pentoxide) was added to the chlorination stage. Residual chlorine in this case was 1.5 lbs. per A.D. ton and viscosity after the alkali treatment was 14.3 cps.

Example II

A spruce sulphite pulp was chlorinated with 34.6 lbs. chlorine per air dry ton of pulp at 25° C. and 3% consistency for one hour. The pulp then received an alkali extraction with 4% NaOH/pulp at 95° C. and 15% consistency for three hours. The viscosity of the

pulp after this stage was 23.2 cps. Another sample of pulp was treated in exactly the same way excepting that 25 p.p.m. V was used in the chlorination; the viscosity in this case was 19.5 cps. A third sample, with 50 p.p.m. V, gave a viscosity of 19.6 cps. These results are typical of the relatively smaller effect obtained in the case of softwood pulp.

Example III

A gum sulphate pulp was chlorinated with 24.6 lbs. chlorine per air dry ton at 25° C. and 3% consistency for one hour and gave a residual of 2.5 lbs. chlorine. The pulp was next given an alkali extraction with 2% NaOH/pulp at 95° C. and 15% consistency for two hours. The viscosity of the pulp after this stage was 23.1 cps. Another sample of the same pulp treated similarly except for 25 p.p.m. V in the chlorination stage gave a chlorine residual of 2.1 lbs. chlorine and had a viscosity after alkali extraction of 13.3 cps. A third sample with 50 p.p.m. V had a chlorine residual of 1.7 lbs. chlorine and a viscosity of 10.5 cps.

Vanadium appears to be unique in the extent of its effect, but other substances such as some compounds of palladium are effective to a much lesser degree. It is interesting to note that when ammonium vanadate is used the presence of the ammonium ion does not inhibit the action of the vanadium. Sodium vanadate probably would be preferred for commercial applications in view of its convenient solubility. It is possible that vanadium pentoxide may be formed in any case under the acid conditions of the chlorination stage. This suggests again that these vanadium compounds may catalyze an oxidation reaction during chlorination. Further, we have not found that vanadium compounds are effective in viscosity reduction under alkaline conditions such as exist in normal hypochlorite bleaching. Vanadium compounds do not seem to be effective in connection with chlorine dioxide bleaching.

Thus it will be seen that this invention provides for the use of vanadium as a catalyst in the chlorination stage of pulp bleaching to reduce pulp viscosity. The use of a catalyst of this nature also enables the pulp to consume more chlorine, and accordingly, overchlorination can be carried out when desired with chlorine residuals of normal amounts. The use of vanadium as a catalyst also enables the normal chlorine demand of a pulp to be consumed more rapidly or it allows more chlorine to be consumed at lower temperatures.

We claim:

1. In the bleaching of cellulose pulp, a process of lowering the viscosity of the cellulose pulp which includes chlorinating the pulp under acid conditions in the presence of a compound of vanadium.

2. In the bleaching of cellulose pulp, a process of lowering the viscosity of the cellulose pulp which includes chlorinating the pulp under acid conditions in the presence of a catalyst selected from the group consisting of sodium vanadate, vanadium pentoxide and ammonium vanadate.

3. In the bleaching of cellulose pulp, a process of lowering the viscosity of the cellulose pulp which includes chlorinating the pulp under acid conditions at a consistency of from about 3% to about 12% and at a temperature of from about 10° C. to about 40° C. in the presence of 10 to 500 parts per million based on the weight of the pulp, of a catalyst selected from the group consisting of sodium vanadate, vanadium pentoxide and ammonium vanadate.

4. The process of claim 2 in which the vanadium is present in an amount from 10 to 500 parts per million based on the weight of pulp.

5. The process of claim 2 in which the vanadium is present in an amount from 10 to 200 parts per million based on the weight of pulp.

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6. The process of claim 2 in which the vanadium is present in an amount from 10 to 50 parts per million based on the weight of pulp.

7. The process of claim 3 in which the pulp consistency is about 3%, the temperature is from 10° C. to 25° C., and the vanadium is present in an amount from 10 to 50 parts per million.

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